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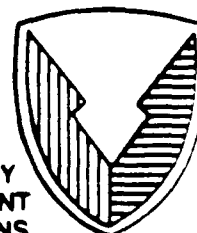# ANOMALOUS ABSORPTION BY ATMOSPHERIC WATER VAPOR AND STABILIZED WATER FOGS IN THE INFRARED AND CM-WAVE REGIONS

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Hugh R. Carlon
U.S. Army Fellow

RESEARCH DIRECTORATE

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Measurements of anomalous or excessive absorption by atmospheric water vapor, i.e., absorption in excess of water monomer absorption and droplet scattering predictions, are analyzed for the infrared and $5-17/cm^{-1}$ regions. Both fair weather and fog data are considered. It is found that observations in both spectral regions can be explained by clustering (hydrogen bonding) of $\sim 10^{-3}$ of vapor molecules. The development leads to several tentative conclusions: (1) equilibrium cluster populations (and maximum absorption) are only attained for vapor in contact with liquid water; (2) the clusters are formed by evaporation, are large, and cannot be modeled by Boltzmann statistics; (3) cluster modes can account for unexplained spectral features at $5-17 cm^{-1}$; (4) excessive absorption both in the infrared and $5-17/cm^{-1}$ regions probably can be explained by the same cluster species. In the appendix, the visible and infrared optical properties of

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evaporation stabilized water fogs also are considered. Evaporation of artificial water fogs can be retarded by the application of coatings of long-chain fatty alcohols to the droplets during generation. Measurements are described, and droplet diameters and mass extinction coefficients are reported for water fogs coated with cetyl alcohol (1-hexadecanol) from a commercial generator. It is shown that droplet size is inversely proportional to the amount of alcohol used and that, while the coatings affect evaporation rate and droplet size, stabilized water fogs otherwise are spectrally similar to uncoated fogs.

PREFACE

The work described in this report was authorized under Project No. 1L161101A91A, In-House Laboratory Independent Research (ILIR). This work was started in January 1978 and completed in December 1982. It was updated by reference to the recent open literature and prepared for publication in December 1988.

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Significant contributions to the work described in the Appendix of this report were made by Roy E. Shaffer of CRDEC, whose earlier research with evaporation-stabilized water fogs provided a starting point for the experimental program discussed here. The author sincerely appreciates the assistance of R. Pritt, C. Townsley, and R. Wright in outfitting and operating the water fog generator system and the assistance of D. Anderson in the aerosol test chamber trials.

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ANOMALOUS ABSORPTION BY ATMOSPHERIC WATER VAPOR AND STABILIZED WATER FOGS

IN THE INFRARED AND CM-WAVE REGIONS

1.   INTRODUCTION

Atmospheric attenuation in excess of predictions, based on absorption by monomeric water molecules and scattering by water droplets, has been measured in the 5-17 cm^{-1} spectral region by <u>Emery, et al[1], hereafter designated as EZG in this report</u>. Similar attenuation is observed in the infrared region, where it is often referred to as the infrared "continuum" absorption of water vapor and can be measured[2] over an interval extending at least from 250-2500 cm^{-1}.

EZG have given experimental data for attenuation in six "window" regions between water monomer absorption lines extending from 5 to 17 cm^{-1}, including data for fog conditions; some of their typical data are shown in Figure 1. Their fog data are reported in such a way that direct comparisons are possible with infrared data known to the author.

Thus, if the excessive water vapor absorption in both spectral regions is compared and can be found to have similar characteristics, clues might be provided to the species responsible for this absorption in both spectral regions. This report presents such an analysis.

2.   METHOD

Some infrared fog data are given in Appendix A. The fog spectra of EZG for the 5 17 cm^{-1} region (Figure 1) are for estimated visibilities of 150 m, 100 m, and 50 m, reading from the bottom (solid) to the top curve. If the mean fog droplet diameter is D_μ (μm), the extinction coefficient is α_λ ($m^2 g^{-1}$) at wavelength λ (μm), and the liquid droplet density is ρ (g cm^{-3}), Carlon[3] has shown that a good approximation exists such that:

$$\alpha_\lambda \sim \frac{3}{D_\mu \rho} \sim \frac{3}{D_\mu} \qquad (D_\mu \gg \lambda) \qquad (1)$$

where ρ can be taken as 1.0 g cm^{-3} in the present discussion. The units conventional to aerosol spectrometry in the visible and in the infrared[4] are used in the Beer-Lambert equation:

$$-\ln T_\lambda = \alpha_\lambda CL \qquad (2)$$

where T_λ is the optical transmittance at wavelength λ, C is the aerosol mass concentration (g m^{-3}), and L is the optical path length (m). Middleton[5] has given the criterion for visibility as T = 0.02. Taking this
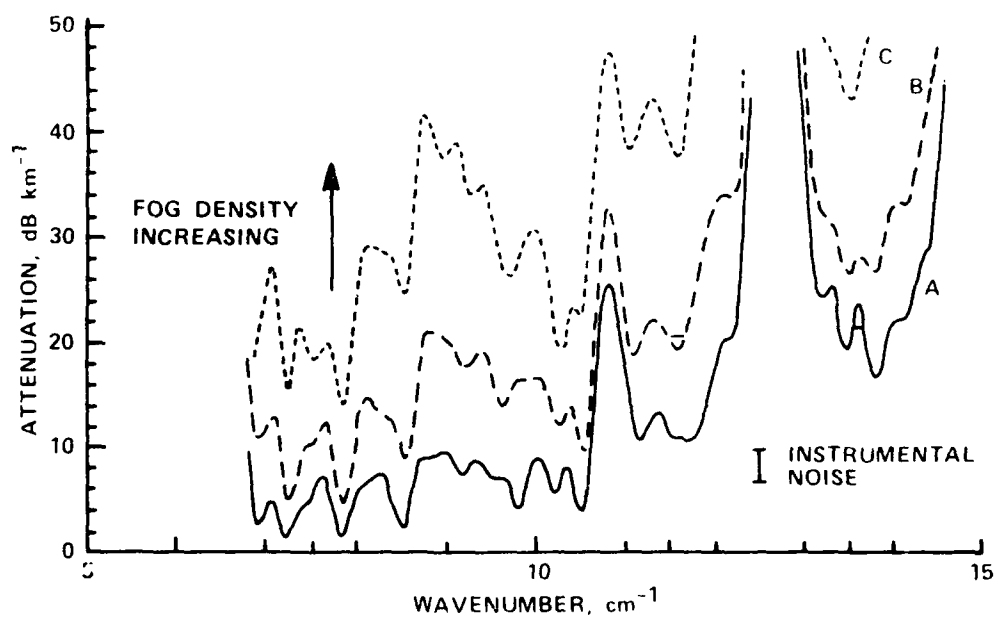
Figure 1. Fog Spectra for the 5-17 cm⁻¹ Region, from Ref. 1, for Estimated Visibilities of 150 m (Curve A), 100 m (Curve B) and 50 m (Curve C).

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v-'ue for the visible wavelengths (λ = 0.4-0.7 μm) and combining Equations (1) and (2) one obtains:

$$3.912 \sim \frac{3}{D_\mu}CL \tag{3}$$

or

$$C \sim 1.304\frac{D_\mu}{L}. \tag{4}$$

EZG presented their fog attenuation data in the units dB km^{-1}; their units can be interchanged with infrared ones by the equation:

$$\frac{dB}{km} = 4343 \ \alpha C. \tag{5}$$

Using Equation (4) and the visibility through the densest fog observed by EZG (L = 50 m), it can be seen that for D_μ = 20 μm (taken as typical by EZG) an upper estimate of fog liquid water content of about 0.5 g m^{-3} is calculated. In the author's experience values of D_μ = 8-10 μm are more typical for developing and young fogs, and from Equation (4) it is readily seen that using C = 0.5 g m^{-3} does, indeed, lead to a conservative upper estimate of attenuation due to droplet scattering by fog particles.

EZG combine this scattering with absorption calculated for water monomers to show (in their Figure 5) that excessive or extra absorption averaging about 10 dB km^{-1} or more was present in windows over the spectral interval 5-14 cm^{-1} in their fog measurements. This extra absorption, combined with observed spectral features which could not be attributed to water monomer, suggested to EZG a molecular (hydrogen-bonded cluster) origin for the extra absorption.

Carlon[6] suggested a very simple test to predict whether molecular absorption by water should be expected in a given wavelength region. The test consists of taking the ratio of absorption coefficients for liquid water to water vapor at a wavelength, $(\alpha_l/\alpha_v)_\lambda$, and taking the magnitude of this ratio as indicative of molecular clustering (hydrogen bonding) and spectral activity in water.

The basis of this test is that liquid water is extensively hydrogen-bonded (clustered), while the unsaturated vapor at normal ambient temperatures is not. Therefore, any absorption coefficient ratios (liquid to vapor) much larger than unity are evidence for spectral absorption due to clustering at the observation wavelength, especially if the ratio varies as the vapor partial pressure varies. Calculations of this ratio for wavelengths from the infrared to the cm waves produce the curves in Figure 2.
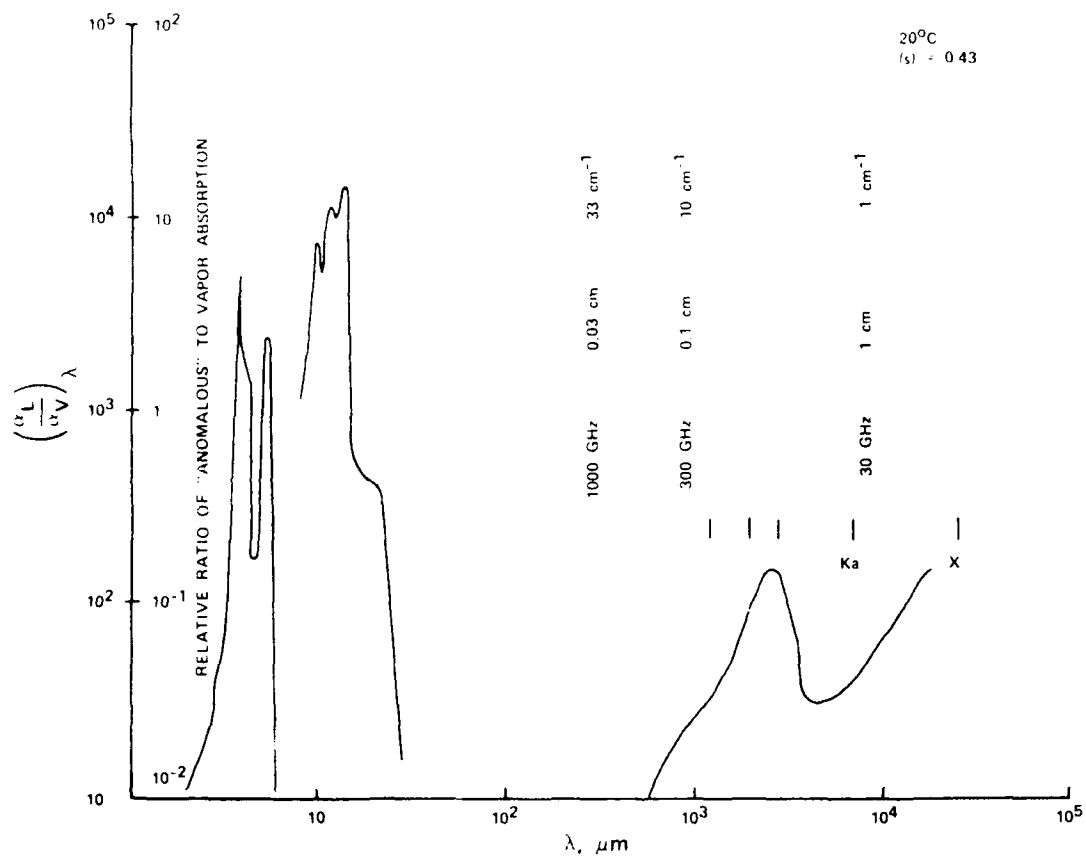
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Figure 2.   Ratio of Absorption by Liquid Water to Absorption by the Same
Quantity of Water Vapor   Over a Broad Spectral Interval.

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For example, at 20°C and a saturation ratio s = 0.43, i.e., **43%** relative humidity, the amplitude of the curves in Figure 2, which have been smoothed, varies widely depending on the value chosen for α_{v_λ}. Although conservative data were used to calculate the ratios in Figure 2, the ratio nonetheless is large near 10 cm^{-1} (λ = 1000 μm) suggesting strong clustering effects there.

Indeed, this ratio in the 8-13 μm infrared window region is very large- greater than 10^4. This is the region of intense infrared continuum absorption, where water vapor and other atmospheric gases have little absorption.

If the extra absorption noted in the infrared continuum, or by EZG, has a molecular origin, and if the ratio $(\alpha_1/\alpha_v)_\lambda$ shown on the ordinate of Figure 2 is indicative of the magnitude of this absorption in liquid water, which is almost completely intermolecularly bonded (hydrogen bonded) compared to the vapor which has far fewer intermolecular bonds, then it seems logical that this ratio should be a measure of the fraction of intermolecular bonding or clustering in the vapor.

For example, measurements of the infrared continuum absorption near 10 μm (Ref. 2) show that this absorption is more than 10 times as intense as the absorption attributable to water monomer (single molecules). If this extra absorption is due, as Bignell[2] himself suggested, to molecular clustering in water vapor, and if the ratio of absorption of clustered water to water vapor (monomer) at 10 μm is about 10^4 (Figure 2), this suggests that the continuum absorption could be due to the clustering of only 10^{-3} of the monomer population in water vapor.

If this same reasoning is applied in the 5-17 cm^{-1} region, i.e., if it is assumed that the same cluster species are responsible for the extra absorption in both the infrared and 5-17 cm^{-1} regions, then it should be useful to compare the levels of extra absorption measured by EZG at 5-17 cm^{-1} to those near 10 μm in the infrared. This is done in the next section.

Also, it is known that the infrared continuum absorption has a quadratic water vapor density dependence[6] like that assumed by EZG for water vapor in the 5-17 cm^{-1} region.

3.   **RESULTS AND DISCUSSION**

EZG have given data for excessive water vapor absorption normalized to a vapor density C_v = 1 g m^{-3} in fair weather (their Figure 3), and for fog conditions assuming a liquid water content C_1 = 0.5 g m^{-3} for a visibility L = 50 m. Average values of fair weather data are given for their six wavenumbers in Table 1. Also given are values of the real (n_λ) and imaginary (k_λ) parts of the complex index of refraction $(n - ik)_\lambda$ at corresponding wavelengths.

The excessive water vapor absorption is given directly in dB km^{-1}, and in "aerosol units" (m^2 g^{-1}) as α_{v_λ}, which is calculated directly from Equation (5) for C_v = 1 g m^{-3}. For comparison, liquid water absorption also is tabulated. The values shown are normalized to EZG's 8.0 dB km^{-1}

Table 1. Computed values from the data of E.Z.G

Wave-number (cm⁻¹)	Wave-length λ(μm)	n_λ	k_λ	Excessive water vapor absorption		Liquid water absorption		Ratio $(\chi_l \chi_v)$	Fraction of vapor clustered $(n_c)_v$
				(dB km⁻¹)	χ_v (m²g⁻¹)	(dB km⁻¹)	χ_l (m²g⁻¹)		
7.3	1370	2.60	1.10	0.09	2.1×10^{-5}	5.6	2.6×10^{-3}	125	8.0×10^{-3}
8.7	1149	2.50	1.00	0.06	1.4×10^{-5}	6.9	3.2×10^{-3}	227	4.4×10^{-3}
10.0	1000	2.48	0.95	0.08	1.8×10^{-5}	8.0	3.7×10^{-3}	204	4.9×10^{-3}
11.6	862	2.40	0.90	0.07	1.6×10^{-5}	9.2	4.2×10^{-3}	263	3.8×10^{-3}
13.9	719	2.35	0.80	0.13	3.0×10^{-5}	13.5	4.8×10^{-3}	161	6.2×10^{-3}
16.0	625	2.30	0.76	0.19	4.4×10^{-5}	17.3	5.5×10^{-3}	125	8.0×10^{-3}
						(averages)		(184)	(5.9×10^{-3})

at 10 cm⁻¹ which assumes $C_1 = 0.5$ g m⁻³ at $L = 50$ m in fog, using Equation (5). Values at other wavelengths were calculated from Ref. 4, using:

$$\alpha_{1_\lambda} \simeq \frac{4\pi k_\lambda}{\lambda \rho} \cdot \frac{9 n_\lambda}{(n_\lambda^2 + k_\lambda^2)^2 + 4(n_\lambda^2 - k_\lambda^2) + 4} \tag{6}$$

which applies only in the Rayleigh scattering regime where D_μ is much smaller than λ. The ratio $(\alpha_1/\alpha_v)_\lambda$ thus is calculated directly, and can be compared to the smoothed curve in the $\lambda = 1000$ μm region of Figure 2. The ratios shown in Table 1 are larger than the conservative values plotted in Figure 1. The average ratio over the spectral interval $\lambda = 625\text{-}1370$ μm (7.3-16.0 cm⁻¹) is 184.

If one makes the assumption that the excessive absorption of water vapor is due to clustered (hydrogen bonded) molecules not unlike those in liquid water, then it follows that the vapor absorption coefficient could be explained as due to a mass or molecular fraction, $(n_c)_v$, of liquid-like molecules clustered in the vapor phase, i.e.

$$\alpha_{v_\lambda} \simeq \frac{(n_c)_v}{(n_c)_1} \alpha_{1_\lambda} \tag{7}$$

or

$$(n_c)_v \simeq (n_c)_1 \frac{\alpha_{v_\lambda}}{\alpha_{1_\lambda}} \tag{8}$$

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where $(n_c)_l$ is the fraction of liquid water that is clustered and its value is known to approach unity at ambient temperatures[7]. $\alpha_{v_\lambda}/\alpha_{l_\lambda}$ is the reciprocal of the ratio shown in Table 1. This vapor cluster fraction is shown in the right-hand column of Table 1 and averages 5.9×10^{-3} over the wavenumber interval investigated by EZG.

This fraction has the same magnitude of about 10^{-3} estimated above for the infrared region near $\lambda = 10$ μm.

If a similar analysis is performed for fog conditions (Figure 1 and EZG's Figure 5) where $L = 50$ m, $C_l = 0.5$ g m^{-3} and $C_v = 5.0$ g m^{-3} (EZG Figure 1), the values shown in Table 2 are computed. Data for 16.0 cm^{-1} were not shown in the EZG fog spectra. In Table 2, an average value of $(n_c)_v = 0.19$ is computed to account for the excessive absorption of water vapor in which liquid water (fog) droplets are present.

Table 2. Fog data of E.Z.G.

Wave-number (cm^{-1})	Wave-length $\lambda(\mu m)$	Excessive water vapor absorption		Ratio $(\alpha_l/\alpha_v)_\lambda$	Fraction of vapor clustered $(n_c)_v$
		(dB km^{-1})	α_v (m^{2}g^{-1})		
7.3	1370	8	3.7×10^{-4}	7.1	0.14
8.7	1149	15	6.9×10^{-4}	4.6	0.22
10.0	1000	17	7.8×10^{-4}	4.7	0.21
11.6	862	21	9.7×10^{-4}	4.3	0.23
13.9	719	17 (est.)	7.8×10^{-4}	6.1	0.16
		(averages)		(5.4)	(0.19)

While this value is large, it nonetheless has the order of magnitude of infrared measurements which suggest that water vapor in contact with liquid water can contain a clustered fraction of several percent or more[8]. Possibly more meaningful is the ratio of average $(n_c)_v$ from Table 2 to that of Table 1 = $0.19/(5.9 \times 10^{-3}) = 32.2$, which suggests that about 30 times more cluster is found in water vapor in the presence of evaporating water (droplet) surfaces than is found in the vapor of typical atmospheres when the humidity does not approach saturation (100% RH).

This was noted as well by EZG, who also suggested that the variability of their data might be explained by variations in the concentration of the species responsible for excessive absorption under these conditions.

The present author concurs completely in this interpretation. The neutral cluster absorption in any wavelength region is proportional to the product of the cluster population per unit volume times the mean or average size of the cluster distribution, according to Carlon[9]. Recent measurements by the author show quite conclusively that as saturation is approached in water vapor, this absorption is enhanced for at least three reasons:

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First, the equilibrium neutral cluster population increases as the square of the saturation ratio, i.e., as s^2. Second, the mean cluster size increases as the square root of s. Third, near-saturation conditions tend to insure the presence of liquid water in the system which permits equilibrium to exist between the evaporating liquid, which is a likely source of the vapor-phase neutral clusters, and the recondensing vapor.

When liquid water is absent from the system or is present in limited quantities, the time history of the vapor becomes significant. That is, the rates of evaporation and cluster decay become predominant in determining cluster populations and sizes, and hence absorption, and equilibrium conditions are not insured. In this light, the extent of "non-equilibrium" discussed by EZG could be considered to be the extent of deviation from saturated conditions.

Because droplet (fog) formation is associated with near-saturation conditions, such that attendant optical scattering results, infrared attenuation due to droplet and cluster absorption are difficult to separate in the infrared wavelengths. But in the 10 cm^{-1} spectral region, scattering corrections are easily made and liquid vs vapor (cluster) absorption can be studied directly.

EZG certainly are not alone in observing anomalous absorption in the cm and mm wavelengths that is far larger than predicted by vapor theory, but that is subject to wide variations in intensity. For example, Rich and Ade[10] reported anomalous absorption, exhibiting no spectral features, that was proportional to water vapor concentration. Furthermore, there was no indication of water dimer absorption lines (as opposed to those of larger clusters), or of any other minor atmospheric species except those due to ozone.

The strong negative temperature dependency of absorption observed by EZG is very dependent upon the temperature dependency of the neutral cluster size distribution. Atmospheric conditions frequently approximate constant partial pressure conditions for time periods ranging from hours to days.

The author has found that as temperature is varied under constant partial pressure conditions, there is an extreme negative temperature dependency of mean cluster size. For example, a saturated water vapor sample at 15°C has an equilibrium neutral cluster distribution with a mean size of about 27 water molecules (monomers) per cluster.

If such a sample is heated at constant partial pressure to, say, 35°C, the mean cluster size is reduced to about 18 monomers. Thus, under common atmospheric conditions approaching or even not deviating greatly from constant partial pressure conditions, the reduced saturation ratio resulting from heating of the vapor will sharply reduce absorption due to the combined effects of reduction in cluster population and size.

If the heating is sufficient to cause drying out of surfaces in the sample space, decay of the neutral cluster populations also will result in the absence of evaporative replenishment, and decidedly non-equilibrium conditions with small absorptions will result. In fogs, nearly perfect

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equilibria are attained and maintained. Accurate modeling of the equilibrium cluster absorption now appears to be a distinct possibility. The author is working on such models, and will communicate any successes in subsequent publications.

If the equilibria associated with excessive absorption in water vapor involve evaporation of liquid water at vapor/liquid interfaces, then the cluster species responsible for this absorption must be phase-transitional ones between those in the vapor and very large ones in the liquid.

Vapor-phase clusters very probably come from the fragmentation of evaporating liquid-phase clusters, rather than from collisions of water monomers as is assumed in kinetic theory thus leading to the expectation of simple Boltzmann cluster size distributions (dimers, trimers, etc.) like those considered by EZG.

If the absorbing clusters are present in water vapor in peaked, statistical size distributions of rather large mean sizes (typically 20-30 monomers), then their behavior cannot be described by simple Boltzmann statistics but is instead far more complex.[8]

4.   CONCLUSIONS

Several significant conclusions can be drawn from this analysis. First, true equilibria of cluster species that cause excessive absorption in water vapor can only be approached under saturated conditions. All other, subsaturated conditions therefore are "non-equilibrium" ones, and can account for the variability of absorption measured by EZG in conditions other than fog.

Thus the absorption of unsaturated atmospheric moist air is dependent upon the availability and time history of its contact with liquid water, which automatically is enhanced as the dew point is approached. But at least in the infrared, this enhanced cluster absorption is difficult to distinguish from extinction due to scattering by large droplets which grow on atmospheric nuclei.

Second, because the absorbing clusters are large, electrically neutral and probably homogeneous ones,[8] their distributions arise from the disintegration of larger liquid-phase clusters at vapor/liquid interfaces, as in evaporation, and their behavior cannot be modeled by Boltzmann statistics but is far more complex. Evaporation can be retarded, as discussed in the Appendix.

Third, modes of distributions of large neutral clusters could account for spectral features noted by EZG in their measurements that could not be explained easily on other grounds.

Fourth, because the fractions of water vapor that must be clustered (about 10^{-3}) to explain excessive or anomalous absorption in the infrared and in the 5-17 cm^{-1} spectral region are about the same, and because the excessive absorption has similar quadratic dependencies in both spectral regions, it seems likely that the same water cluster species can

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account for excessive absorption in both regions although their modes accounting for this absorption in the two regions will be, of course, decidedly different.

LITERATURE CITED

1.   Emery, R.J., Zavody, A.M., and Gebbie, H.A., "Measurements of Atmospheric Absorption in the Range 5-17 cm-1 and its Temperature Dependence," J. Atmos. Terr. Phys. 42, 801 (1980).

2.   Bignell, K.J., "The Water-Vapour Infra-Red Continuum," Q. Jl. R. Met. Soc. 96, 390 (1970).

3.   Carlon, H.R., "Mass Extinction Coefficients Estimated for Nonabsorbing Spherical Aerosol Particles in the Geometric Scattering Regime," Appl. Opt. 19, 1891-1892 (1980).

4.   Carlon, H.R., "Aerosol Spectrometry in the Infrared," Appl. Opt. 19, 2210-2218 (1980).

5.   Middleton, W.E.K., Vision Through the Atmosphere, p 105, University of Toronto Press, Toronto, 1952.

6.   Carlon, H.R., "Phase Transition Changes in the Molecular Absorption Coefficient of Water in the Infrared: Evidence for Clusters," Appl. Opt. 17, 3192-3193 (1978).

7.   Luck, W.A.P., "Spectroscopic Studies Concerning the Structure and the Thermodynamic Behaviour of H_2O, CH_3OH and C_2H_5OH," Discuss. Faraday Soc. 43, 115, 132 (1967).

8.   Carlon, H.R., "Infrared Water Vapor Continuum Absorption: Equilibria of Ions and Neutral Water Clusters," Appl. Opt. 20, 1316-1322 (1981).

9.   Carlon, H.R., "Limits of Detection for Condensation Nuclei Counters," J. Appl. Phys. 53(9), 6492-6493 (1982).

10.   Rice, D.P., and Ade, P.A.R., "Absolute Measurements of the Atmospheric Transparency at Short Millimetre Wavelengths," Infrared Phys. 19, 575-584 (1979).

APPENDIX

*OPTICAL PROPERTIES (0.63-13μm) OF WATER FOGS STABILIZED AGAINST EVAPORATION BY LONG-CHAIN ALCOHOL COATINGS.

A1.   INTRODUCTION

The Beer-Lambert equation is:

$$- \ln T_\lambda = \alpha_\lambda C L \qquad (A1)$$

where T_λ is the optical transmittance at wavelength λ, α_λ is the mass extinction coefficient (m^2/g) at that wavelength, C is the mass (aerosol) concentration (g/m^3), and L is the optical path length in meters.

Most water fogs have significant optical extinction coefficients at all wavelengths from 0.63 to beyond 13 μm.[1] Typical values of α_λ are 0.3-0.5 m^2/g at λ = 0.63 μm, 1.0-1.5 m^2/g at 3-5 μm and 0.15-1.0 in the 7-13 μm wavelength region, where a minimum of 0.15 m^2/g is typical near λ = 11 μm.

Heavy fogs seriously reduce optical range not only in the visible wavelengths but in the infrared as well. For example, a typical natural fog having a droplet mass concentration of C = 0.1 g/m^3 will cause complete loss of visibility of a black object on a white background at a range of only 100-130 m (Ref. 2), and a comparable infrared extinction at λ = 10 μm over a range of 200-300 m.

If water fog evaporation can be retarded sufficiently, the fog can be used in diverse applications including blanketing of frost-threatened crops with a radiative barrier, or military electrooptical screening. Chamber and field tests have been performed to obtain extinction coefficients for coated fogs produced by a commercial generator marketed briefly by a subsidiary of the Boeing Company under the trade name "FROSTOP"(**).

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* Originally published by Carlon, H.R., and Shaffer, R.E., <u>Journal of Colloid and Interface Science</u> 82, 203-207 (1981); presented here in updated form.

** Manufactured by Boeing Aerospace Company, Seattle, Washington 98124 under subsidiary Applied Technology Corporation, 6361 1st Avenue South, Seattle, Washington 98108.

The FROSTOP system was designed to generate evaporation-stabilized water fogs to protect crops and orchards against freezing.

A2.   EQUIPMENT DESCRIPTION

The FROSTOP system consists of a gasoline-driven air compressor and 6-10 generator units, each comprising a water tub with a float-operated water inlet valve, a submersible propane burner, and ancillary handware for connection of air, fuel, and makeup water lines to each generator unit.

Each propane burner is housed in two concentric metal sleeves, with the flame enclosed on all sides except for the bottom of the housing. Once the burner is lighted, the sleeves are turned downward into the water tub and the hot gases are carried by an airstream into the water, where vigorous bubbling occurs and the water is heated to an operating temperature of about 94°C.

This is hot enough to melt bricks of cetyl alcohol (containing an emulsifier) that are dropped into the generator tubs and quickly become uniformly mixed throughout the hot water bath. The hot gases bubbling through the water thus carry heavy concentrations of water vapor and alcohol to the surfaces of the water baths, where cooling and condensation occur and steam-like clouds of alcohol-coated water droplets become fully developed about 1 m above the tubs under typical atmospheric conditions.

In Figure A1 three tubs (generators) are shown in operation, connected by hoses to the gasoline-powered compressor in the lower-right foreground. The propane fuel storage tank and a spare generator also can be seen at the lower right.

Cetyl alcohol (1-hexadecanol) has a 16-carbon chain and a melting point of 50°C allowing it to dissolve readily in the hot water baths. Longer-chain alcohols such as stearyl (18 carbons) and eicosyl (20 carbons) also melt well below the 94°C bath temperature and, because of their greater chain lengths, produce still greater retardation of evaporation than does cetyl alcohol. However, the longer-chain molecules cause complications in droplet lifetimes, and in costs and availabilities of the alcohols.

Each generator tub can produce 113 kg (250 lb) of stabilized water fog per hour, and requires (hourly) 136 liters (36 gal) of water, 13 liters (3.5 gal) of liquid propane fuel, 0.45 kg (1 lb) of cetyl alcohol/emulsifier brick, and 93 m^3 (3300 ft^3) of air from the compressor.

A3.   EXPERIMENTAL PROCEDURE

The FROSTOP system was set up outdoors with one generator tub shrouded so that the water fog could be drawn directly into an aerosol optical test chamber for characterization. In this way fog samples could be physically and spectrally analyzed while visual observations, photographs (Figure A1), and motion pictures were made of clouds outside the chamber building under various meteorological conditions.

Figure A1.   FROSTOP System in Operation.

Instrumentation in the test chamber[1] included a scanning infrared radiometer covering the 3-5 μm and 8-13 μm wavelength regions, a He:Ne laser operating at 0.63 μm, a modified spectrometer operated at 1.06 μm as a transmissometer, gravimetric samplers to determine droplet mass concentration at specific times, and aerosol impactors for rough determinations of fog droplet size distributions that were also checked using optical techniques reported earlier.[3]

The chamber optical path was L = 6.0 m and was monitored continuously by the He:Ne laser while the radiometer scanned the infrared wavelengths. Periodically, the radiometer scan was stopped at λ = 10 μm for transmittance readings.

After a test cloud was generated, measurements were taken four or more times as the water fog dissipated over a 20-30 minute time period. In different tests, different cetyl alcohol concentrations were used and these directly affected fog droplet size and optical extinction.

A4.   RESULTS AND DISCUSSION

Results of the tests are shown in the table following.

TABLE

Optical Extinction Coefficients of Coated Water Fogs

Fog droplet mass concn, C (g/m³)	Mean droplet diameter (μm)	Rel. hum. (%)	Extinction coef., α_x	
			λ = 0.63 μm	λ = 10 μm
0.72	8	100	0.37	0.19
0.55	9	100	0.36	0.20
0.34	8	100	0.43	0.21
0.18	7	100	0.46	0.18
0.37	2-3	70	0.85	0.12
0.37	2-3	70	0.88	0.12
0.36	2-3	70	0.85	0.12
0.18	2-3	94	0.76	0.12
0.12	2-3	94	0.83	0.11
0.23	<1	91	1.74	0.05
0.12	~1	91	~2.6	~0.12
0.92	4	41	0.58	0.13
0.74	7	88	0.48	0.20
0.50	6-7	88	0.41	0.16
0.29	3-4	90	0.40	0.07
0.11	3-4	~100	0.91	0.18
0.11	3	~100	0.63	0.09

In none of the radiometer spectra was any evidence found of the cetyl alcohol coating material, as was expected because of the very thin molecular coatings generated onto the droplets. A typical water fog spectrum is shown in Figure A2, for fog droplets having mean diameters of 6-7 μm.
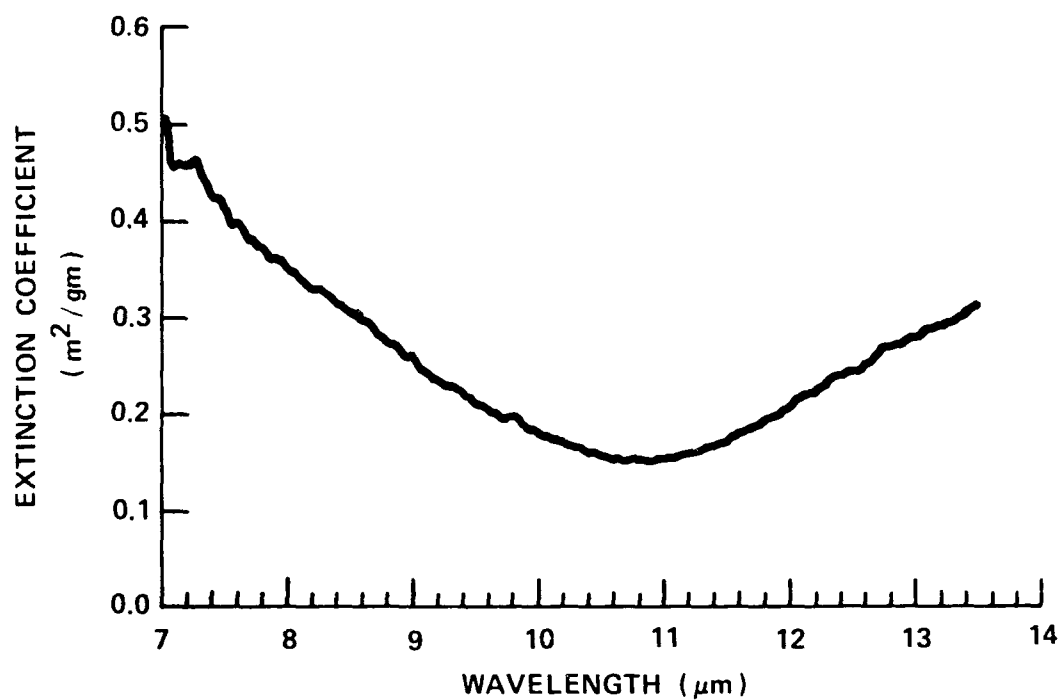
Figure A2. Spectrum of Extinction Coefficient, α_λ, for an Alcohol-Coated Water Fog with Droplets of 6-7 μm Mean Diameter.

There is no evidence of a cetyl alcohol absorption band near $\lambda =$ 9.4 μm. The two most signii̇i̇c̈n̈ẗ observations were (1) that while the alcohol coatings affect evaporation rate and droplet size, coated water fogs otherwise are similar spectrally to uncoated fogs, and (2) that droplet size is inversely proportional to the amount of coating material used, at least for fogs produced by the FROSTOP system.

The table shows that the extinction coefficients, α_λ, for larger droplets generated using a minimum of alcohol in the generator tub are nearly identical to those for natural or steam-generated, unstabilized water fogs at the same wavelengths. For the stabilized fogs, droplet approximation techniques[3] for mass concentration and mean diameter work very well.

When an excess of alcohol was used in the generator bath, the water vapor rising from the water surface had proportionately higher con- centrations of alcohol in it. The table indicates that newly condensed coated droplets became stabilized at diameters inversely proportional to the alcohol concentration used. Figure A3 is a composite of data showing these trends.

The (presumed) monolayer curve shows the spectrum of α_λ for fogs coated with the manufacturer's recommended alcohol concentration given earlier. The curve labeled "XS cetyl" shows the spectrum obtained when several alcohol/emulsifier bricks were added to the generator bath. Spectra for all other trials summarized in the table would lie between these extremes.

While a few trends relating droplet diameter to time were noted in these trials, it was impossible to obtain definitive data on the evapora- tion rate of stabilized water fogs vs relative humidity (RH). Due to limited chamber volume and the rapid rise in RH when water fogs were introduced, even relatively dry starting conditions quickly were altered.

However, droplets generated into the chamber at lower humidities always were smaller than those generated into vapor-saturated chamber air. In most tests, mean droplet diameter increased with RH for several minutes, and then decreased as the RH fell when fog generation into the chamber ceased.

In summary, trials showed that either low ambient RH or high alco- hol content in the FROSTOP generator bath would produce stabilized water fog droplets smaller than the 8-10 μm mean diameter typical of new droplets with no or minimal coatings in vapor-saturated air.

Presumably this occurs because under low ambient humidity condi- tions condensing droplets are reevaporating as the alcohol coating is con- densing on them, while in the case of high alcohol concentrations the coating seals the droplets before they are fully grown.

Droplet evaporation, and its effect on the extinction coefficient of an aerosol cloud, has been investigated and modeled for water and a variety of other substances by several authors.[4]
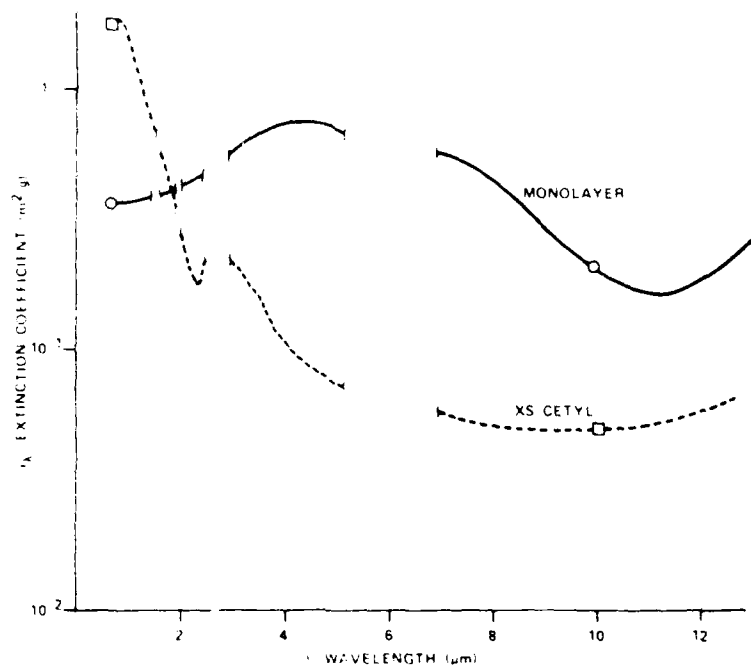
Figure A3. Composite Spectra of the Extremes of the Extinction
Coefficient α_λ for Coated Water Fogs Generated Under
Different Conditions.

A5.   CONCLUSIONS

The spectra of artificial water fogs stabilized against evaporation by cetyl alcohol coatings range from those which are very similar to spectra of natural water fogs, to those for very small particle fogs that extinguish (scatter) radiation strongly in the visible wavelengths but have little extinction at longer infrared wavelengths.

The latter fogs result when alcohol/water concentration ratios are high during fog generation, and/or when ambient humidities are well below saturation during generation. In no case was the alcohol absorption band near $\lambda = 9.4$ µm observed in spectra of the stabilized water fogs (e.g., Figure A2) indicating that the alcohol coatings on the droplets were very thin and, presumably, were molecular monolayers as other parameters in the generation process would seem to indicate.

For example, each generator tub produces 113 kg of stabilized fog per hour per 0.45 kg of alcohol/emulsifier brick, a ratio of 250:1. It seems likely that evaporation-stabilized water fogs could be generated by systems smaller in scale than FROSTOP, perhaps by using steam and alcohol mist or carrier streams to form droplets in predetermined size ranges.

LITERATURE CITED

1.   Carlon, H.R., Anderson, D.H., Milham, M.E., Tarnove, T.L., Frickel, R.H., and Sindoni, I., "Infrared Extinction Spectra of Some Common Liquid Aerosols," Appl. Opt. 16, 1598-1605 (1977).

2.   Middleton, W.E.K., "Vision Through the Atmosphere," University of Toronto Press, Toronto, p. 105 (1952).

3.   Carlon, H.R., Milham, M.E., and Frickel, R.H., "Determination of Aerosol Droplet Size and Concentration From Simple Transmittance Measurements," Appl. Opt. 15, 2454-2456 (1976).

4.   Tsang, T.H., and Korgaonkar, N., "Effect of Evaporation on the Extinction Coefficient of an Aerosol Cloud," Aerosol Sci. Technol. 7, 317-328 (1987).